

WO 02/16271 A1



For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.

TITLE OF THE INVENTION

METHOD FOR TREATING METAL CONTAMINATED WATER

BACKGROUND OF THE INVENTION

5 The invention relates to a process for treating contaminated water to precipitate metals without increasing the total dissolved solids content. In particular, the invention relates to a process for cleaning water contaminated with hexavalent chrome.

 To clean water contaminated with hexavalent chrome, the chrome must
10 be reduced to its trivalent state prior to precipitation. Hexavalent chrome reduction typically occurs at pH around 3 using an acid, such as sulfuric acid, and a reducing agent (such as sulfur dioxide, ferrous sulfate, sodium metabisulfite, sodium bisulfite, electrolyte iron). The reduction step is followed by a neutralization step which
15 consists of adjusting the pH of the acidic contaminated water to a higher pH to precipitate the trivalent chrome and to meet the discharge permit conditions. The required pH for the chrome precipitation is between 6.5 and 8.2. The most common alkaline reagent for raising the pH is sodium hydroxide. This is due to its high and immediate solubility in water. These two characteristics result in a reduction in the plant equipment sizes since little residence time is required to achieve the required
20 pH. However, the same two characteristics cause the total dissolved solids (TDS) of the treated water to dramatically increase. The high TDS in the treated water is a problem since there are typically limits on the amount of permitted discharge. To reduce the TDS in the treated water stream, ultrafiltration, microfiltration, and reverse osmosis are used. These processes result in the concentration of the salt (TDS) in
25 a small percentage of the treated stream (around 10%) and produce a filtrate with acceptable levels. The concentrated reject stream remains a problem. Crystallizers or evaporators are also used to further reduce the reject stream volume. The evaporation and filtration units are very expensive, hard to operate, require large space areas for installation, and have a high energy requirement for operation. To eliminate these
30 expensive unit operations, a chemical process which will not cause an increase in the TDS of the treated stream and produce chromium free water is needed.

 U.S. Patent No. 6,096,223, which issued on August 1, 2000 discloses a similar process using calcium hydroxide or oxide to adjust the pH of the solution following treatment of the water with the soluble ferrous ions.

Thus, there exists a need for a safe, environmentally sound process for the cleaning of metal contaminated water without raising the TDS in the treated water.

SUMMARY OF THE INVENTION

5 The present invention relates to a process for treating contaminated water to precipitate metals resulting in no increase in the total dissolved solids. The metals should be in a valent state that require reduction or oxidation to achieve the insoluble state. The insoluble state can be achieved by mixing the contaminated water with an electron donor or receiver to alter the metal from its soluble valent state into
10 its insoluble valent state. These metals include chromium (VI & III), arsenic (V & III), phosphorous (V & III), silicon (IV & VI), manganese IV & VII, copper (II & I), cobalt (III & II) and nickel (II & III). For example, chromium VI is very soluble in water and needs to be reduced in order to be transformed to chromium III which is insoluble in water. The reduction occurs at low pH (below 7) and the precipitation
15 of chrome III occurs at high pH (above 7). This invention relates to a process for cleaning the contaminated water without increasing the total dissolved solids (TDS) that usually occur due to the chemical addition to adjust the pH. In particular, the invention relates to the use of phosphoric acid and magnesium hydroxide to adjust the pH of chromium contaminated water during the treatment process without increasing
20 the total dissolved solids (TDS).

BRIEF DESCRIPTION OF THE DRAWINGS

Figure 1 shows a schematic illustration of one embodiment of the total electrochemical process.

25 Figure 2 shows a comparison of different acids and bases tested for the process of treating contaminated groundwater.

DETAILED DESCRIPTION OF THE INVENTION

30 The present invention relates to a process for treating contaminated water to precipitate metals without increasing the total dissolved solids content. In particular, the invention relates to the use of phosphoric acid and magnesium hydroxide to adjust the pH of chromium contaminated water during the treatment process without increasing the total dissolved solids (TDS).

The process comprises the steps of:

35 a. collecting the contaminated water;

- 5 b. lowering the pH to below 7 in an on-line acid tank;
 c. mixing the contaminated water with an electron donor
 or electron receiver to switch the contaminant from its
 soluble valent state into its insoluble valent state;
 d. adjusting the pH of the contaminated water to above 7 to
 allow for precipitation of contaminants and added species; and
 e. collecting and processing the precipitated sludge.

Further processing of the water then takes place as hereinafter described.

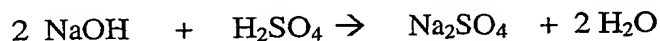
10 In a preferred embodiment, there is disclosed a process for treating
chromium contaminated water comprising the steps of

- a. collecting the contaminated water;
 b. lowering the pH to below 7 in an on-line acid tank;
 c. mixing soluble ferrous ions with the contaminated water
15 to reduce the hexavalent chromium to its trivalent state;
 d. adjusting the pH to above 7 to allow for precipitation
 of the contaminant; and
 e. collecting and processing the precipitated sludge.

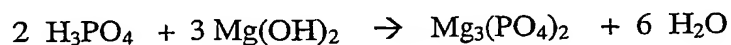
20 It has been found that by using phosphoric acid in place of sulfuric
acid, the industry standard, and magnesium hydroxide instead of sodium hydroxide,
the TDS is significantly lowered.

 It has been shown that the use of sodium hydroxide and sulfuric acid
results in the formation of sodium sulfate as shown in the following reaction:

25



 Sodium sulfate is very water soluble and consequently causes the TDS to increase.
 By using magnesium hydroxide and phosphoric acid, it results in the formation of
30 magnesium phosphates which are not as soluble and do not increase the TDS. This
is shown in the following equation:



In the treatment of chromium contaminated water, electrochemical treatment is one method of reducing the hexavalent chromium to trivalent chromium. Electrochemical treatment operations consists of reduction of the chromium VI in an acidic pH (about 3.2 when sulfuric acid is used) using an electron donor such as iron, zinc, silver or any other metal that can donate electrons to reduce the hexavalent chromium. In a preferred embodiment, soluble ferrous ions are used in the reduction. The iron is usually produced off-line by an electrochemical cell using sacrificial electrodes and sulfuric acid, as represented by the following equation:



Using a slight excess of the stoichiometric 3.2 pounds of iron per pound of chromium, the ferrous ions are mixed with the contaminated water. In the resulting redox reaction, hexavalent chromium is reduced to the insoluble trivalent state and divalent iron is oxidized to its insoluble trivalent state at an acidic pH (about 3), as represented by the following equation:

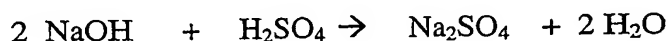


The slight excess of ferrous ions, adjusted pH and sufficient residence time drive the reaction to completion. After the reaction is completed, the pH is adjusted to a slightly alkaline state (about 8.4) using sodium hydroxide to allow precipitation of the metal ions in a pH adjustment tank. It should be noted here that when sulfuric acid is used, a pH of 3.3 or below must be achieved for the reduction of the chromium VI to occur. When sodium hydroxide is used to elevate the pH, a pH of 8.3 or above must be achieved to precipitate the resultant chromium III. Additionally, an amount greater than the stoichiometric ratio of iron to chromium should be used (3.6 gm of iron/gm of chrome).

After the electrochemical treatment, the stream is advanced to a clarifier where a polyelectrolyte polymer is added to promote coagulation of the reduced metal which settles at the bottom of the clarifier. Solids are drawn from the bottom of the clarifier and allowed to settle in a gravity thickener followed by a plate and frame filter press. The treated water is pH adjusted to below 8 and polished with multimedia filters and carbon, prior to reinjection to the aquifer.

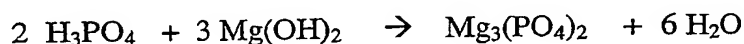
The water is continually checked for total dissolved solids and total chromium concentration. The chrome concentration is continuously kept below 30 PPB; however, the total dissolved solids (TDS) oscillate between 1100 to 1400 PPM, depending on the plant TDS influent concentration which ranges from 400-700 PPM and the chromium influent concentration which ranges between 5,000 PPB and 25,000 PPB.

As noted above, one of the main reasons for the increase in the total dissolved solids is the addition of caustic sodium hydroxide to raise the pH from 3 to 8. The sodium hydroxide is very soluble in water and reacts with the sulfuric acid as shown in the following equation:



The sodium sulfate formed is very water soluble and consequently causes the Total Dissolved Solids to increase from about 500 to 1150 PPM.

It has been found that by replacing the sulfuric acid with phosphoric acid and the sodium hydroxide with magnesium hydroxide, the resultant chemistry is



Magnesium phosphates are not soluble in water and consequently the total dissolved solids will not increase. It should be noted here that when phosphoric acid is used to lower the pH, the reduction of chromium VI did not depend on the acidic pH of the solution. The reduction reaction of chromium occurred even at pH of about 6. When magnesium hydroxide was used to lower the pH, the precipitation of chromium III did not depend on the alkalinity of the solution. Even at pH 7.5, the precipitation occurred. In addition, the reduction reaction of chromium VI occurred even when below stoichiometric ratios of iron was used (about 1.6 gm of iron/gm of chrome). This may be due to the formation of chromium phosphates which are insoluble in water.

In the process of the invention, any type of phosphoric acid such as pyrophosphoric acid, metaphosphoric acid, polyphosphoric acid, superphosphoric acid or nonorthophosphoric acid may be used. Phosphoric acid of any purity, food grade, industrial grade, fertilizer grade or unrefined green grade is acceptable. In the

process, the phosphoric acid has a P_2O_5 concentration between about 1% to about 80%, preferably about 20% to about 45%.

The magnesium hydroxide used in step d. to raise the pH from about 3 to about 8 can be added in slurry form or solid form. Alternatively, magnesium oxide
5 can be used because it converts to magnesium hydroxide upon contact with the water. These can be of any purity or grade. The magnesium source is used in the mixed slurry at a concentration of between about 1% to about 50%, preferably about 18% to about 25%.

Figure 1 illustrates a general schematic flow diagram of the entire
10 process including the processing of the precipitated sludge.

The following example illustrates, without limiting, the scope and spirit of the invention.

EXAMPLE 1

15 Experiments were performed to compare the magnesium/phosphoric system to sodium/phosphoric, magnesium/sulfuric, calcium/sulfuric and sodium/sulfuric systems and the effects of the different systems on the amount of TDS in the treated groundwater. Each experiment was performed using chromium contaminated
20 groundwater (3.4 PPM). Electrolyte iron in sulfuric acid was added to each sample at 3.5 gm iron/gm chrome. The pH of the water was lowered using sulfuric acid to a pH of 3.2. After stirring for 5 minutes at the acidic pH, the pH of the solution was raised to 8 using the different salts (magnesium hydroxide, sodium hydroxide and calcium hydroxide). The solution was then filtered to separate the precipitant, and the clear
25 liquid was analyzed for chromium and TDS using the methods mentioned above. It was found that the use of calcium hydroxide with phosphoric acid generated no additional total dissolved solids. The contaminated water and the treated water contained approximately the same amount of total dissolved solids (412 ppm) since magnesium phosphate is not soluble in water. The chromium analysis showed the
30 water has a chromium concentration below 10 ppb in all cases.

Figure 2 summarizes the results of the experiments.

35 The principles, preferred embodiments and modes of operation of the present invention have been described in the foregoing specification. However, the invention which is intended to be protected is not to be construed as limited to

the particular embodiments disclosed. The embodiments are to be construed as illustrative rather than restrictive. Variations and changes may be made without departing from the spirit of the present invention. Accordingly, all such variations and changes which fall with the spirit and scope of the present invention, as defined

5 in the following claims, are expressly intended to be embraced thereby.

WHAT IS CLAIMED IS:

1. A process for treating contaminated water to precipitate metals comprising
 - a. collecting the contaminated water;
 - b. lowering the pH to below 7 in an on-line acid tank;
 - c. mixing the contaminated water with an electron donor or electron receiver to switch the contaminant from its soluble valent state into its insoluble valent state;
 - d. adjusting the pH of the contaminated water to above 7 to allow for precipitation of contaminants and added species; and
 - e. collecting and processing the precipitated sludge.
2. The process of Claim 1 wherein phosphoric acid is used in step b to lower the pH of the water to below 7.
3. The process of Claim 2 wherein phosphoric acid of any purity, food grade, industrial grade, fertilizer grade or unrefined green grade is used.
4. The process of Claim 3 wherein the phosphoric acid has a P_2O_5 concentration between about 1% to about 80%.
5. The process of Claim 4 wherein the phosphoric acid has a P_2O_5 concentration between about 20% to about 45%.
6. The process of Claim 2 wherein the phosphoric acid used to lower the pH in step b is pyrophosphoric acid, metaphosphoric acid, polyphosphoric acid, superphosphoric acid or nonorthophosphoric acid.
7. The process of claim 1 wherein magnesium hydroxide or magnesium oxide is used in step d to raise the pH from about 3 to about 8.
8. The process of claim 7 wherein magnesium hydroxide is added in slurry form or solid form.

9. The process of claim 7 wherein magnesium oxide is added in solid form or slurry form.

10. The process of claim 9 wherein magnesium oxide or magnesium hydroxide is of any purity or grade.

11. The process of claim 7 wherein the concentration of magnesium hydroxide or magnesium oxide in the mixed slurry is between about 1% to about 50%.

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12. The process of claim 11 wherein the concentration of magnesium hydroxide or magnesium oxide in the mixed slurry is between about 18% to about 25%.

13. The process of claim 1 wherein the electron donor or receiver used is iron, zinc, silver, aluminum or any other metal that can donate or receive electrons to alter the contaminating metal from its soluble valent state to its insoluble valent state.

14. The process of Claim 13 wherein soluble ferrous ions are used to alter the valent state of the contaminating metal.

15. A process for treating chromium contaminated water comprising

- a. collecting the contaminated water;
- b. lowering the pH to below 7 in an on-line acid tank;
- c. mixing soluble ferrous ions with the contaminated water to reduce the hexavalent chromium to its trivalent state;
- d. adjusting the pH of the contaminated water to above 7 to allow for precipitation of the contaminant; and
- e. collecting and processing the precipitated sludge.

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16. The process of Claim 15 wherein phosphoric acid is used in step b to lower the pH of the water to below 7.

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17. The process of Claim 16 wherein phosphoric acid of any purity, food grade, industrial grade, fertilizer grade or unrefined green grade is used.

18. The process of Claim 15 wherein the phosphoric acid has a
5 P_2O_5 concentration between about 1% to about 80%.

19. The process of Claim 18 wherein the phosphoric acid has a P_2O_5 concentration between about 20% to about 45%.

20. The process of Claim 16 wherein the phosphoric acid used to lower the pH in step b is pyrophosphoric acid, metaphosphoric acid, polyphosphoric acid, superphosphoric acid or nonorthophosphoric acid.

21. The process of Claim 15 wherein magnesium hydroxide or
15 magnesium oxide is used in step d to raise the pH to above 7.

22. The process of Claim 21 wherein the magnesium hydroxide or magnesium oxide is added in slurry form or solid form.

23. The process of Claim 21 wherein magnesium oxide or
20 magnesium hydroxide is of any purity or grade.

24. The process of claim 21 wherein the concentration of magnesium hydroxide or magnesium oxide in the mixed slurry is between about
25 1% to about 50%.

25. The process of claim 24 wherein the concentration of magnesium hydroxide or magnesium oxide in the mixed slurry is between about
30 18% to about 25%.

26. A process for treating chromium contaminated water comprising
a. collecting the contaminated water in a groundwater storage tank;
b. lowering the pH to below 7 with phosphoric acid in an on-line
35 acid tank;

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- c. mixing soluble ferrous ions with the contaminated water to reduce the hexavalent chromium to its trivalent state;
- d. adjusting the pH of the contaminated water to above 7 with magnesium oxide or hydroxide to allow for precipitation of the contaminant; and
- e. collecting and processing the precipitated sludge.

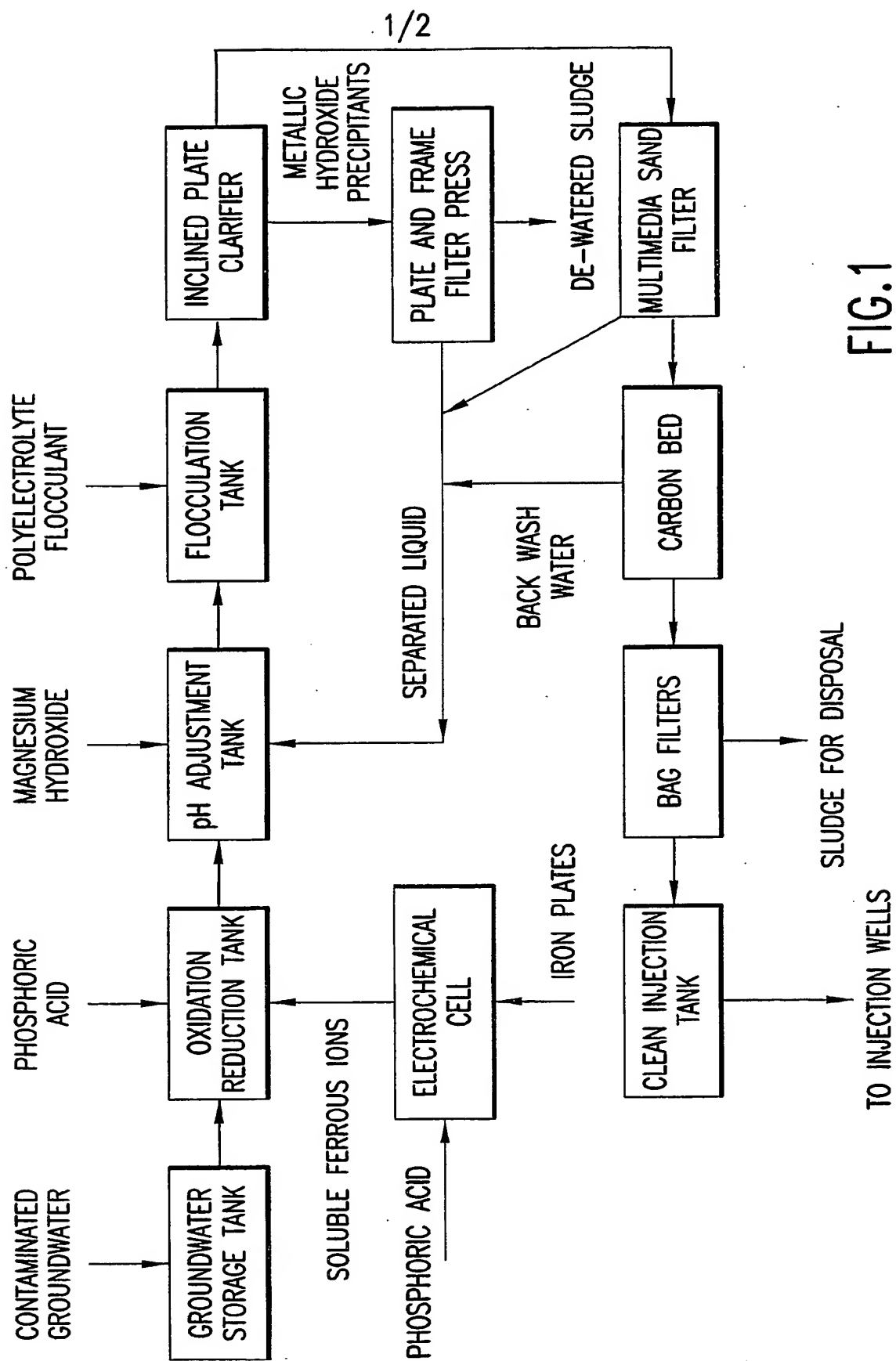


FIG.1

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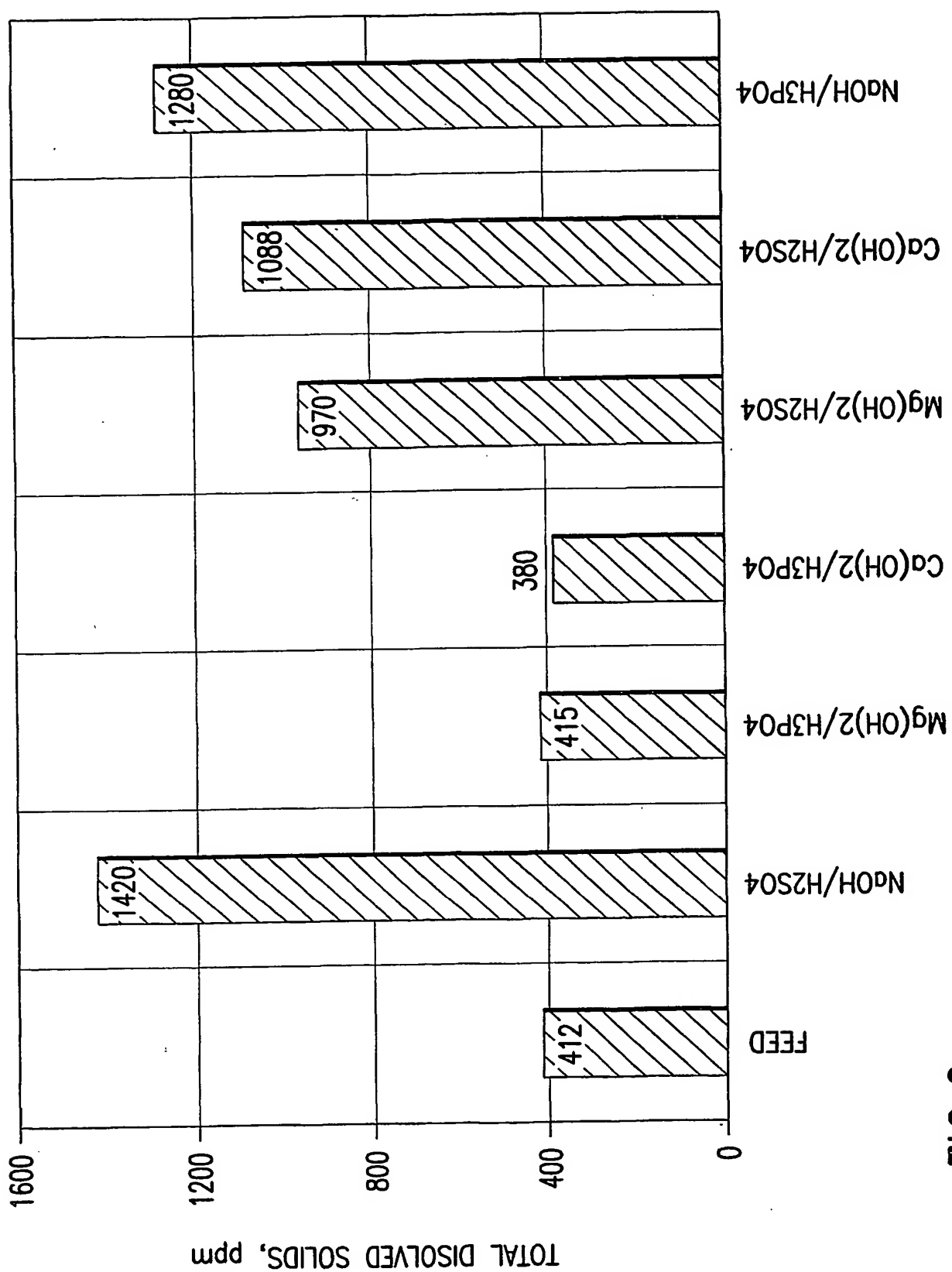


FIG.2

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US01/25453

A. CLASSIFICATION OF SUBJECT MATTER

IPC(7) :C02F 1/62

US CL :210/720, 724, 752, 913

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

U.S. : 210/720, 724, 752, 913

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 5,000,858 A (MANNING et al) 19 March 1991, entire document.	1, 7, 13 - 25, 21, 23, 26
X	US 5,158,687 A (TERRY et al) 27 October 1992, entire document.	1-25
X	US 4,671,882 A (DOUGLAS et al) 09 June 1987, entire document.	1-6



Further documents are listed in the continuation of Box C.



See patent family annex.

* Special categories of cited documents:	"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
"A" document defining the general state of the art which is not considered to be of particular relevance	"X" document of particular relevance: the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
"E" earlier document published on or after the international filing date	"Y" document of particular relevance: the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)	"&" document member of the same patent family
"O" document referring to an oral disclosure, use, exhibition or other means	
"P" document published prior to the international filing date but later than the priority date claimed	

Date of the actual completion of the international search

03 NOVEMBER 2001

Date of mailing of the international search report

28 NOV 2001

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INTERNATIONAL SEARCH REPORT

International application No.
PCT/US01/25453

Box I Observations where certain claims were found unsearchable (Continuation of item 1 of first sheet)

This international report has not been established in respect of certain claims under Article 17(2)(a) for the following reasons:

1. ☐ Claims Nos.:
because they relate to subject matter not required to be searched by this Authority, namely:

2. ☐ Claims Nos.:
because they relate to parts of the international application that do not comply with the prescribed requirements to such an extent that no meaningful international search can be carried out, specifically:

3. ☐ Claims Nos.:
because they are dependent claims and are not drafted in accordance with the second and third sentences of Rule 6.4(a).

Box II Observations where unity of invention is lacking (Continuation of item 2 of first sheet)

This International Searching Authority found multiple inventions in this international application, as follows:

1. ☐ As all required additional search fees were timely paid by the applicant, this international search report covers all searchable claims.
2. ☐ As all searchable claims could be searched without effort justifying an additional fee, this Authority did not invite payment of any additional fee.
3. ☐ As only some of the required additional search fees were timely paid by the applicant, this international search report covers only those claims for which fees were paid, specifically claims Nos.:

4. ☐ No required additional search fees were timely paid by the applicant. Consequently, this international search report is restricted to the invention first mentioned in the claims; it is covered by claims Nos.:

Remark on Protest

- ☐ The additional search fees were accompanied by the applicant's protest.
☐ No protest accompanied the payment of additional search fees.

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